PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C03C 13/06 A1

(11) International Publication Number: WO 90/02713

(43) International Publication Date: 22 March 1990 (22.03.90)

(21) International Application Number: PCT/DK89/00205

(22) International Filing Date: 4 September 1989 (04.09.89)

(30) Priority data:
4923/88 5 September 1988 (05.09.88) DK

(71) Applicant (*for all designated States except US*): ROCKWOOL INTERNATIONAL A/S [DK/DK]; Hovedgaden 501, DK-2640 Hedehusene (DK).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*) : MOGENSEN, Gurli [DK/DK]; Egevej 78, Vemmedrup, DK-4632 Bjæverskov (DK).

(74) Agent: LEHMANN & REE; Frederiksberg Allé 26, DK-1820 Frederiksberg C (DK).

(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FI, FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent), US.

Published
*With international search report.*

(54) Title: MINERAL FIBRES

(57) Abstract

Fibres with the following composition: $SiO_2$ 47-54 % by weight, $Al_2O_3$ 4-7.5 % by weight, $Fe_2O_3$ 1-8.5 % by weight, CaO 10-24.5 % by weight, MgO 10-21 % by weight, $Na_2O$ 0.1-10 % by weight, $K_2O$ 0.1-1.5 % by weight soluble in salt solutions.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|---|---|---|---|---|---|
| AT | Austria | ES | Spain | MG | Madagascar |
| AU | Australia | FI | Finland | ML | Mali |
| BB | Barbados | FR | France | MR | Mauritania |
| BE | Belgium | GA | Gabon | MW | Malawi |
| BF | Burkina Fasso | GB | United Kingdom | NL | Netherlands |
| BG | Bulgaria | HU | Hungary | NO | Norway |
| BJ | Benin | IT | Italy | RO | Romania |
| BR | Brazil | JP | Japan | SD | Sudan |
| CA | Canada | KP | Democratic People's Republic of Korea | SE | Sweden |
| CF | Central African Republic | | | SN | Senegal |
| CG | Congo | KR | Republic of Korea | SU | Soviet Union |
| CH | Switzerland | LI | Liechtenstein | TD | Chad |
| CM | Cameroon | LK | Sri Lanka | TG | Togo |
| DE | Germany, Federal Republic of | LU | Luxembourg | US | United States of America |
| DK | Denmark | MC | Monaco | | |

Mineral fibres

The present invention relates to a novel type of mineral fibres.

Conventional mineral fibres are produced from naturally occuring materials and therefore the costs of raw materials are relatively low.

Such known mineral fibres typically have the following composition:

| | | | |
|---|---|---|---|
| $SiO_2$ | about | 45 | % by weight |
| $Al_2O_3$ | - | 13.5 | - |
| FeO | - | 5.5 | - |
| CaO | - | 20.5 | - |
| MgO | - | 10.5 | - |
| TiO | - | 1.0 | - |
| $Na_2O + K_2O$ | - | 2.5 | - |

The known mineral fibres are characterized by their high temperature resistance, but they are only slightly affected by salt solutions. Therefore they degrade very slowly when deposited at a tip or in other places in nature after use.

The specification of NO patent application No. 874323 (Manville Corporation) describes inorganic fibres serving as a substitute for conventional mineral wool fibres and containing MgO in an amount of 0.1-30 % by weight and $Al_2O_3$ in an amount of 0-10 % by weight in addition to $SiO_2$ and CaO. According to the above-mentioned patent application said fibres, which are mainly characterized in having a relatively low content of $Al_2O_3$, are considerably more soluble in salt solutions than conventional mineral fibres, e.g. in the so-called Gamble's solution, i.e. an aqueous solution containing the following salts in a dissolved form:

| Component | Concentration g/l |
|---|---|
| $MgCl_2 . 6H_2O$ | 0.160 |
| NaCl | 6.171 |
| KCl | 0.311 |

| | |
|---|---|
| $Na_2HPO_4$ | 0.149 |
| $Na_2SO_4$ | 0.079 |
| $CaCl_2$, $2H_2O$ | 0.060 |
| $NaHCO_3$ | 1.942 |
| $NaC_2H_3O_2$ | 1.066 |

An essential drawback of the known soluble fibres is that they are produced from relatively expensive oxides and not from naturally occuring raw materials.

Furthermore some of the known fibres have a relatively poor heat resistance and are consequently unsuitable for use at high temperatures.

Surprisingly it has been found that mineral fibres with a considerably greater solubility in salt solutions than the above-mentioned known mineral fibres, and which at the same time exhibit an acceptable high temperature resistance can be produced from naturally occuring raw materials and other inexpensive raw materials.

Mineral fibres according to the invention are characterized in having the following composition:

| | | |
|---|---|---|
| $SiO_2$ | 47-54 | % by weight |
| $Al_2O_3$ | 4-7.5 | - |
| $Fe_2O_3$ | 1-8.5 | - |
| CaO | 10-24.5 | - |
| MgO | 10-21 | - |
| $Na_2O$ | 0.1-10 | - |
| $K_2O$ | 0.1-1.5 | - |

the total content of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ not exceeding 65 % by weight.

Mineral fibres of the above-mentioned composition can be produced from naturally occuring raw materials and other readily obtainable and inexpensive materials such as waste products from the production of mineral wool fibres and glass. Examples of such raw material compositions are listed in Table I.

Table I

Raw material composition

| | | | |
|---|---|---|---|
| 1 | | Diabase | 70 % |
| | | Cement briquettes[1)] | 30 % |
| 2 | | Diabase | 20 % |
| | | Clay briquettes[2)] | 80 % |
| 3 | | Cement briquettes[3)] | 80 % |
| | | Olivine-containing diabase | 20 % |
| | | Clay briquettes consisting of: | |
| 4 | | Clay | 45 % |
| | | Sand | 22 % |
| | | Olivine sand | 22 % |
| | | Rasorite (Sodium borate) | 8 % |
| | | Blast-furnace slag | 8 % |
| | | Iron oxide | 3 % |
| | | Clay briquettes consisting of: | |
| 5 | | Clay | 50 % |
| | | Rock wool waste | 10 % |
| | | Lime | 20 % |
| | | Sand | 10 % |
| | | Olivine sand | 10 % |
| | | Clay briquettes consisting of: | |
| 6 | | Clay | 50 % |
| | | Lime | 20 % |
| | | Sand | 10 % |
| | | Olivine sand | 10 % |
| | | Soda | 10 % |
| | | Cement briquettes consisting of: | |
| 7 | | Olivine | 53 % |
| | | Glass waste from the production of glass bottles | 35 % |

Cement 12 %

1) Consisting of 12 % cement, 40 % mineral wool waste, 5 % dolomite and 43 % diabase.

2) Consisting of 50 % clay, 30 % mineral wool waste, 15 % olivine sand and 5 % iron oxide slag.

3) Consisting of 15 % cement, 23 % mineral wool waste, 22 % sand, 10 % olivine sand, 30 % olivine-containing diabase.

The solubility of the mineral fibres of the invention and known fibres has been examined by storing fibre samples weighing 830 mg in 250 ml of said Gamble's solution for 5 hours at a temperature which was increased from 37°C to 60°C and by measuring the $SiO_2$-concentration of the solution at the end of the test.

The results obtained will appear from Table II.

Table II

| | Known Mineral Fibres | | Mineral fibres according to the invention | | | |
|---|---|---|---|---|---|---|
| Composition | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 |
| $SiO_2$ | 44.6 | 49.0 | 50.5 | 54.2 | 50.8 | 47.2 |
| $Al_2O_3$ | 13.3 | 10.3 | 5.8 | 5.9 | 6.2 | 6.9 |
| $TiO_2$ | 1.1 | 2.2 | 0.6 | 0.4 | 0.4 | 0.4 |
| $Fe_2O_3$ | 6.1 | 8.0 | 7.9 | 5.0 | 2.3 | 3.0 |
| CaO | 20.3 | 14.3 | 11.8 | 9.8 | 24.4 | 20.7 |
| MgO | 10.6 | 11.8 | 20.0 | 17.0 | 12.7 | 14.4 |
| $Na_2O$ | 2.0 | 1.7 | 0.2 | 2.2 | 0.5 | 6.5 |
| | 0.5 | 1.6 | 0.5 | 1.1 | 1.3 | 0.7 |
| $B_2O_3$ | | | | 3.2 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Solubility, ppm | | | | | | |
| $SiO_2$ | 3.74 | 1.84 | 8.22 | 4.79 | 12.88 | 10.80 |

As will appear from the above Table II the mineral fibres according to the invention have a considerably higher solubility in the salt solution than the conventional known fibres.

A fibre sample according to NO patent application No. 874323 was subject to a similar examination. The fibres had the following composition:

| | |
|---|---|
| $SiO_2$ | 50.2 % by weight |
| $Al_2O_3$ | 10.0 - |
| $TiO_2$ | 0.3 - |
| $Fe_2O_3$ | 0.7 - |
| CaO | 27.9 - |
| MgO | 6.8 - |
| $Na_2O$ | 0.2 - |
| $K_2O$ | 0.7 - |

A solubility corresponding to a $SiO_2$-concentration of 3.16 ppm was measured which is also considerably less than the solubility of the fibres of the invention.

It could be feared that mineral fibres with a relatively high solubility in salt solutions would be sensitive to heat and therefore would be unsuitable for use at high temperatures and that they lack the necessary fire resistance. However, tests have shown that this fear is groundless in respect of the fibres according to the invention.

The tests were carried out with mineral fiber samples weighing from 0.5 to 1 g. These samples were placed on a refractory plate and then inserted into an oven which was preheated to a given temperature. After 30 minutes in the oven at this given temperature the fibre samples were removed from the oven and examined. If the dimensions,

structures and elasticity of the fibres were unchanged this was taken as an indication of the fibres being resistant at the given temperature.

If it was found that the fibres were brittle (sintered), a new sample was subject to a similar treatment at a temperature which was 25°C below the one tried first.

If necessary the test was repeated with a further reduction of the temperature until the fibres remained unchanged.

The examination of the mineral fibres according to the invention (tests 3-6) listed in Table II showed that they were all resistant at a temperature higher than 750°C which corresponds to the temperature resistance of the mineral fibre sample according to NO patent application No. 874323.

Mineral fibres according to the invention with a composition within the following limits:

| | | |
|---|---|---|
| $SiO_2$ | 47-51 | % by weight |
| $Al_2O_3$ | 5-7 | - |
| $Fe_2O_3$ | 2-4 | - |
| CaO | 15-21 | - |
| MgO | 10-15 | - |
| $Na_2O$ | 0.5-7 | - |
| $K_2O$ | 0.5-1.5 | - |

exhibit a particularly high solubility in salt solutions.

Patent claims

1. Mineral fibres, characterized in having the following composition:

| | | |
|---|---|---|
| $SiO_2$ | 47-54 | % by weight |
| $Al_2O_3$ | 4-7.5 | - |
| $Fe_2O_3$ | 1-8.5 | - |
| CaO | 10-24.5 | - |
| MgO | 10-21 | - |
| $Na_2O$ | 0.1-10 | - |
| $K_2O$ | 0.1-1.5 | - |

2. Mineral fibres according to claim 1, characterized in having the following composition:

| | | |
|---|---|---|
| $SiO_2$ | 47-51 | % by weight |
| $Al_2O_3$ | 5-7 | - |
| $Fe_2O_3$ | 2-4 | - |
| CaO | 15-21 | - |
| MgO | 10-15 | - |
| $Na_2O$ | 0.5-7 | - |
| $K_2O$ | 0.5-1.5 | - |

# NTERNATIONAL SEARCH REP[illegible]

International Application No PCT/DK89/00205

## I CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [illegible]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

C 03 C 13/06

## II FIELDS SEARCHED

Minimum Documentation Searched [illegible]

| Classification System | Classification Symbols |
|---|---|
| IPC 4 | C 03 C |
| US Cl | 106 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [illegible]

SE, NO, DK, FI classes as above

## III DOCUMENTS CONSIDERED TO BE RELEVANT [illegible]

| Category * | Citation of Document, [illegible] with indication, where appropriate, of the relevant passages [illegible] | Relevant to Claim No [illegible] |
|---|---|---|
| A | US, A, 2 576 312 (LEONARD JOHN MINNICK) 27 November 1951 | |
| A | GB, A, 2 152 026 (INSTITUT FUR MINERALISCHE ROHSTOFF-UND LAGERSTATTENWIRTSCHAFT) 31 July 1985 | |
| A | DE, A1, 3 222 546 (MENGEL, KURT, DR) 5 May 1983. | |

* Special categories of cited documents: [illegible]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV CERTIFICATION

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
|---|---|
| 1989-11-15 | 1989 -12- [illegible] |
| International Searching Authority | Signature of Authorized Officer |
| Swedish Patent Office | May Hallne |

Form PCT/ISA/210 (second sheet) (January 1985)